PATENT SPECIFICATION

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(54) APPARATUS FOR THE SYNTHESIS OF AMMONIA

(71) We, HALDOR TOPSØE A/S, a Danish Company, of 55 Nymøllevej, 2800 Lyngby, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to apparatus which can be used in the synthesis of ammonia at elevated pressure and temperature.

Synthesis of ammonia is conducted by passing a stream of synthesis gas comprising three parts of hydrogen and one part of nitrogen through a catalyst arranged in one or more beds in a converter operated at elevated pressure and temperature. However, even if the concentrations of hydrogen and nitrogen in the synthesis gas are close to being stoichiometric with respect to ammonia formation, complete reaction to ammonia cannot be obtained by one passage of the process stream through the converter. The reason is that the equilibrium concentration of ammonia in a stoichiometric synthesis gas at normal operating conditions is below 20%, and typically from 15 to 18%, by volume. Therefore, after most of the ammonia has been removed from the stream of synthesis gas leaving the converter, the remaining synthesis gas with a residual concentration of ammonia is recycled to the converter together with fresh synthesis gas.

The cost of the energy required for compressing and recycling synthesis gas is an important factor in ammonia production. This means that great savings can be achieved by an increase in the amount of ammonia which, at a given set of operating conditions, is produced per unit volume of synthesis gas passed through the catalyst. In other words, a high ammonia concentration in the stream of synthesis gas from the catalyst is important for the economy of an ammonia process.

The synthesis of ammonia is an exothermic reaction, which means that the temperature of the synthesis gas will increase while it passes through the catalyst. This increasing temperature will displace the equilibrium concentration towards lower ammonia concentration. It is therefore important to limit the temperature increase by cooling either the catalyst or the synthesis gas. Several methods for providing such cooling are known.

British Patent Specifications No. 1,204,634 disclosed arranging the catalyst in the converter in two or more separate catalyst beds and introducing cold synthesis gas between the beds. This can be done simply. However, this method has the disadvantage that the partly reacted synthesis gas is diluted with unreacted synthesis gas, which means that the ammonia concentration of the stream of synthesis gas from the last catalyst bed is reduced.

Dilution of the partly reacted synthesis gas can be avoided by another cooling method based on indirect cooling. For this purpose, one or more heat exchangers are built into the converter, either directly in a catalyst bed or between the separate catalyst beds. In this way, cooling can be achieved by circulating through such heat exchangers cold synthesis gas which is thereby heated for use in the ammonia synthesis process. The cooling medium used in such heat exchangers can alternatively be water under pressure, which is afterwards used for steam generation.

However, the method of indirect cooling has hitherto not been very widely used industrially. This is primarily because the incorporation of a heat exchanger and associated pipes which allow the cooling medium to pass to and from the heat exchanger is space-consuming. Particularly when the indirect heat exchange is based on steam generation, the necessary equipment is complicated because the cooling water has to pass through the converter shell to

and from an external steam generator.

We have now found that the above problems can be reduced or eliminated by conducting ammonia synthesis in a new converter in which the synthesis gas is cooled between the catalyst beds by indirect heat exchange with cooler synthesis gas, using a heat exchanger occupying a minimum of space and offering easy operation.

According to the invention, apparatus suitable for use in the synthesis of ammonia comprises a vessel containing first and second catalyst beds through which a process stream of synthesis gas can pass radially in series, the beds being annular and arranged on a common annular axis; a heat exchanger positioned on the said axis in the centre of one of the catalyst beds; a first inlet for a first stream of synthesis gas; a second inlet for an exchange stream of synthesis gas and means whereby the exchange stream can pass to the heat exchanger; and means whereby the first stream and the exchange stream can be combined to form the process stream (which is cooled in the heat exchanger by the exchange stream).

It is particularly preferred that the shell of the vessel should be cooled by a shell stream of synthesis gas, in which case means are provided for the shell stream to pass inside the vessel and outside the catalyst beds. In this case, the exchange stream can be drawn directly from the shell stream or a further inlet can be provided for the shell stream and the first stream, the exchange stream and the shell stream can be combined to form the process stream.

The shell of the vessel will usually be substantially cylindrical. Each catalyst bed will usually be mounted between inner and outer concentric perforated walls and two plates secured to the perforated walls at opposite ends of those walls.

The first stream of synthesis gas, the exchange stream of synthesis gas and, if provided and if separate from the exchange stream, the shell stream of synthesis gas are usually caused to be combined on the axis of the annuli. It will be appreciated that the first stream can be used to adjust the temperature of the process stream, the exchange stream having cooled the heat exchanger and any shell stream having cooled the vessel shell.

In order to provide optimum process conditions, a larger amount of catalyst is required in the second catalyst bed through which the process stream passes than in the first catalyst bed. The second catalyst bed is therefore usually longer than the first catalyst bed.

The heat exchanger in the centre of one of the catalyst beds may be of the type having a plurality of parallel tubes, through which the exchange stream passes, or of any other type which serves the same purpose, e.g. the lamella type.

The invention will now be described by way of example with reference to Figures 1 to 6 of the accompanying drawings, each of which is a schematic representation of different embodiments of converter apparatus according to the invention in longitudinal sectional view.

Figure 1 illustrates a converter having a shell 11, an inlet 12 for the shell stream of synthesis gas, an inlet 13 for the exchange stream of synthesis gas, an inlet 14 for the first stream of synthesis gas and an outlet 15 for the product stream of synthesis gas. The first catalyst bed 21 and the second catalyst bed 22 surround, respectively, a heat exchanger 41 and a central transfer pipe 42. A heat exchanger 61, distinct from the essential heat exchanger 43, is provided. In order to facilitate removal for inspection and maintenance of the essential parts of the converter, i.e. the catalyst beds, the central heat exchanger and the central transfer pipe, as well as the heat exchanger 61, the converter shell has a removable shell closure 16.

Both catalyst beds have a hollow central cylindrical space around their common axis. The first catalyst bed 21 is annular and is mounted between two concentric perforated walls; an inner wall 23 and an outer wall 24. These perforated walls are secured at their lower ends to a plate 25 which retains the catalyst in the first catalyst bed. The perforated walls are secured at their upper ends to a plate 26 which serves to retain the catalyst in the second catalyst bed 22. In order to facilitate loading and unloading of the catalyst in the first catalyst bed 21, the plate 26 is provided with removable lids (not shown) which can be opened when the second catalyst bed is emptied.

The second catalyst bed 22 is also annular and is mounted between two concentric perforated walls, an inner wall 27 and an outer wall 28. The perforated walls are secured at their lower ends to the plate 26 and at their upper ends to a plate 29. The plate 29 can be entirely removed during loading and unloading of the catalyst, or parts of it can be opened.

Between the heat exchanger 41 and the inner perforated wall 23 is an annular space 52 through which the process stream from the first catalyst bed passes. The cooling medium, the exchange stream, passes through the central transfer pipe 42 and through the tubes 43 of the heat exchanger 41 while the process stream from annular space 52 flows around the tubes of the heat exchanger so that the process stream is cooled before it passes to the second catalyst bed 22. Between the central transfer pipe 42 and the inner perforated wall 27 is an annular space 53 which receives the process stream from the second catalyst bed 22.

A cylindrical sheet 31 provides an annular space 55 along the converter shell 11 for the shell stream of synthesis gas introduced through inlet 12 and an annular space 54 around the catalyst beds. Another cylindrical sheet 32 surrounds the first catalyst bed 21 and provides an

annular space 51. There are further passageways allowing the shell stream of synthesis gas from the annular space 55 to pass through the heat exchanger 61 to the annular space 51. While passing through these passageways, the shell stream of synthesis gas combines with the first stream of synthesis gas introduced through the inlet 14 and the exchange stream of synthesis gas to form the process stream of synthesis gas which passes through the first catalyst bed 21. The passageways for each of the three feed streams of synthesis gas meet at a point on the common axis of the catalyst beds. From this point, the process stream of synthesis gas is directed radially outwards through a radial passage to the outside of the first catalyst bed. The radial passage serves to mix the feed streams, thereby reducing or eliminating any temperature variation in the synthesis gas introduced to the first catalyst bed.

The apparatus illustrated in Figure 2 is similar to that illustrated in Figure 1 except that the shell stream of synthesis gas subsequently serves as the exchange stream. Consequently, inlet 13 has been omitted and the central pipe 42 is positioned so that the shell stream can pass directly to the heat exchanger 41 where it serves as the exchange stream. In addition, the heat exchanger 61 illustrated in Figure 1 has been omitted.

Figure 3 illustrates apparatus similar to that of Figure 2 except that the heat exchanger 41 is mounted in the centre of the second catalyst bed 22 and the central transfer pipe 42 is mounted in the centre of the first catalyst bed 21. The shell stream of synthesis gas passes directly to the heat exchanger 41 and the central transfer pipe 42 allows the exchange stream to pass to the point at which it is combined with the first stream of synthesis gas. The annular space 53 is located between the inner wall 27 and the heat exchanger 41, and the annular space 52 is located between the inner wall 23 and the central transfer pipe 42.

The apparatus illustrated in Figure 4 is similar to that illustrated in Figure 1 except that the first catalyst bed 21 is mounted above the second catalyst bed 22, the plate 26 retaining the material of the first bed and the plate 25 that of the second bed. This relative position of the catalyst beds has simplified the passageways for the various streams of synthesis gas, relative to the embodiment of Figure 1, the sheet 32 being omitted since it is not required for the provision of annular space 51.

Figure 5 illustrates apparatus similar to that of Figure 4 except that the passageways have been rearranged to provide inward flow of the process stream through the second catalyst bed 22, i.e. from annular space 54 through the bed to annular space 53. Accordingly, separate plates *26a* and *26b* replace the plate 26 in Figure 4 and the annular sheet 32 is included in order to provide the annular space 51 around the first catalyst bed 21.

Figure 6 illustrates apparatus similar to that of Figure 5 except that a bottom heat exchanger 61 is provided. In the embodiments of Figures 5 and 6, the presence of the two separate plates *26a* and *26b* which provide a passageway between the two catalyst beds 21 and 22 further provides the possibility of separate removal of the first catalyst bed 21 with the heat exchanger 41 from the converter for inspection, maintenance or catalyst replacement.

The manner in which the illustrated apparatus of the invention can be used to effect synthesis of ammonia at elevated pressure and temperature will now be described. A shell stream is introduced through inlet 12, an exchange stream (if separate from the shell stream) through inlet 13, and a first stream through inlet 14. When no heat exchanger 61 is present, the shell stream may subsequently serve as the exchange stream although, even when no heat exchanger 61 is present, it may be preferable for flexibility of operation to have separate shell stream and exchange stream inlets. It is essential to provide separate shell stream and exchange stream inlets when heat exchanger 61 is present.

The process stream of synthesis gas, which by suitable adjustment of the rates and temperatures of the first stream, the exchange stream and any separate shell stream, has a temperature suitable for passing through the catalyst in the first catalyst bed, is passed from annular space 51 radially inwards from annular space 51 to the annular space 52. The process stream of synthesis gas is then passed through the hot side of the heat exchanger 41 so that it is cooled by indirect heat exchange with the exchange stream of synthesis gas before being passed to annular space 53 (Figures 1, 2, 3 and 4) or annular space 54 (Figures 5 and 6). The process stream of synthesis gas is then passed radially through the second catalyst bed 22, and a product stream of synthesis gas is obtained in annular space 54 (Figures 1, 2, 3 and 4) or annular space 53 (Figures 5 and 6).

The following Examples illustrate the use of the apparatus of this invention.

Example 1

Converter apparatus as illustrated in Figure 1 is used in an ammonia plant having a production capacity of 1,000 metric tons of ammonia per day.

The two catalyst beds are loaded with an ammonia synthesis catalyst having a particle size of 1.5-3 mm. Catalyst volumes are 12 m^3 in the first catalyst bed 21 and 29 m^3 in the second catalyst bed 22. The composition of the synthesis gas available for the various bed streams is given in Table I together with the composition of the product stream and further data related to this Example 1. The converter is operated at a pressure of about 270 kg/cm^2 g.

A shell stream of synthesis gas of 151,480 Nm^3/hr., having a temperature of about 120°C, is introduced through the inlet 12. The shell stream is first passed through the annular space 55, where it serves to provide adequate cooling of the converter shell for protection against too high temperatures. Thereafter, the shell stream is passed to the bottom heat exchanger 61. Here the shell stream is heated by indirect heat exchange with the product stream which afterwards leaves the converter through the outlet 15.

An exchange stream of synthesis gas of 191,450 Nm^3/hr., having a temperature of about 120°C, is introduced through the inlet 13 and via the central transfer pipe 42 passes through the central heat exchanger 41. Here the exchange stream serves to cool the process stream passed from the first catalyst bed 21 to the second catalyst bed 22. The exchange stream leaves the central heat exchanger at a temperature close to the reaction temperature and is combined with the shell stream from the bottom heat exchanger 61.

A first stream of synthesis gas, at 40,000 Nm^3/hr., having a temperature of about 120°C, is introduced through the inlet 14. At a position along the common axis of the two catalyst beds, the by-pass stream combines with the shell stream and the exchange stream to form a process stream of synthesis gas of 382,930 Nm^3/hr., having a temperature of 360°C. The relative amounts of the three streams which form the process stream can be adjusted during operation to obtain the desired temperature at the inlet to the first catalyst bed 21.

Via the annular space 51 the process stream is passed through the first catalyst bed 21, where its temperature is increased to 520°C because of the exothermic reaction, which causes the ammonia concentration to increase from 3.5 to 14.4 vol.%. While subsequently passing through the central heat exchanger 41, the process stream is cooled to 390°C and via the annular space 53 passed through the second catalyst bed 22 under heating to 472°C, while the ammonia concentration increases to 20.8 vol.%. The product stream of synthesis gas is then received in the annular space 55 and passed through the bottom heat exchanger 61 for cooling and thereafter through the outlet 15 at about 360°C.

EXAMPLES 2-6

Data for further examples on conducting ammonia synthesis in accordance with this invention are given in Table I. The Examples 2-6 are similar to Example I, except that they are conducted in the other embodiments of the converter as illustrated in Figures 2 to 6. The results are given in Table II.

TABLE I

Example		1-6
Embodiment of Converter, Fig.		1-6
Production Capacity of Converter, metric tons/day		1,000
Catalyst Volume, m^3		
First Bed		12
Second Bed		19
Stream Composition, vol.%		
Feed Stream, inlet first bed,	H_2	63.4
	N_2	21.1
	NH_3	3.5
	inerts	12.0
Feed Stream, outlet first bed,	H_2	54.2
	NH_2	18.1
	NH_3	14.4
	inerts	13.3
Product Stream, outlet second bed,	H_2	48.9
	N_2	16.3
	NH_3	20.8
	inerts	14.0

TABLE II

Example	1	2	3	4	5	6
Embodiment of Converter (Fig.)	1	2	3	4	5	6
Stream Rates (Nm^3/h)						
Shell Stream	151,480	322,930	322,930	322,930	322,930	131,480
Exchange Stream	191,450					211,450
By-pass Stream	40,000	60,000	60,000	60,000	60,000	40,000
Total Process Stream, inlet first bed	382,930	382,930	382,930	382,930	382,930	382,930
Product Stream, outlet converter	328,090	328,090	328,090	328,090	328,090	328,090
Stream Temperature (°C)						
Feed Streams, inlet converter	110	237	237	237	237	150
Process Stream, inlet first bed	360	360	360	360	360	360
Process Stream, outlet first bed	520	520	520	520	520	520
Process Stream, inlet second bed	390	390	390	390	390	390
Process Stream, outlet second bed	472	472	472	472	472	472
Process Stream, outlet converter	345	472	472	472	472	385

As can be seen from Examples 1 and 6, the bottom heat exchanger 61 serves to cool the product gas before it leaves the converter through the outlet 15 of the converter shell. Without this cooling the product gas will leave the converter shell at much higher temperatures. Although such high temperatures require a more careful selection of heat resistant materials of construction, the bottom heat exchanger is omitted in cases, as in Examples 2 to 5, where it is desirable to utilize the heat of the product gas for production of high pressure steam.

An essential economic advantage of the converter of this invention is that it is possible to obtain a high production of ammonia per unit volume of synthesis gas passed through the catalyst beds. This high production is achieved as a result of the cooling without dilution of the process stream of synthesis gas between the two catalyst beds combined with the possibility of obtaining the desired temperature for the process stream as it enters each catalyst bed. For an optimum performance of the ammonia synthesis catalyst it is imperative that the temperatures of each catalyst bed can be independently selected. This is possible in the converter of this invention because of the flexibility in changing the relative rates of the different streams of synthesis gas.

This advantages of the converter of this invention can be further illustrated by curves showing the variations in temperature and ammonia concentration as the process stream of synthesis gas is passing through the two catalyst beds. In Fig. 7, curve A represents the thermodynamic equilibrium concentration at the conditions of pressure and synthesis gas composition used in Example 1. Curve B illustrates an approach to this equilibrium by 10 C degrees corresponding to a reasonable approach, which can be obtained in practice.

The remaining curves in Fig. 7 represent changes occurring in the temperature and the ammonia concentration of the process stream of synthesis gas during its passage through the catalyst beds for two different cases. One case, represented by the solid line, corresponds to the conditions of Example 1. In this case, the synthesis gas is introduced into the first catalyst bed at a temperature of 360°C and has an ammonia concentration of 3.5%. While the process stream is passing through the first catalyst bed, these two parameters will change along the solid line 1-2, so that at the outlet of the first catalyst bed the temperature is 520°C and the ammonia concentration is 14.4%. Before being introduced into the second catalyst bed, the process stream of synthesis gas is cooled by indirect heat exchange, which means that the parameters will change along the solid line 2-3*a* (ammonia concentration is kept constant). At the inlet to the second catalyst bed, the temperature is 390°C and the ammonia concentration is 14.4%.

While the process stream is passing through the second catalyst bed, the parameters will change along the solid line 3*a*-4, so that at the outlet of the second catalyst bed the temperature is 472°C and the ammonia concentration is 20.8%.

The other case, represented by the dotted line in Fig. 7, corresponds to conditions similar to those used for Example 1, except that, instead of cooling the process stream between the catalyst beds by indirect heat exchange, the cooling is effected by direct quench. This has no effect on the first catalyst bed and the parameters will again change along the solid line 1-2. During the cooling, however, the ammonia concentration will decrease because the cooling gas added to the synthesis gas from the first catalyst bed has a lower ammonia concentration. Accordingly, the parameters will change along the dotted line 2-3*b*. At the inlet to the second catalyst bed the temperature is 390°C but, because of the dilution, the ammonia concentration is only 10.5%. During the passage through the second catalyst bed, the parameters will change along the dotted line 3*b*-4 and, at the outlet of the second catalyst bed, the temperature is 493°C and the ammonia concentration 18.0%.

The curves shown in Fig. 7 illustrate the advantage of conducting ammonia synthesis using the converter of the present invention. As a result of the invention the production of ammonia per unit volume of synthesis gas passed through the catalyst beds can be significantly increased with respect to known apparatus.

WHAT WE CLAIM IS:

1. Apparatus suitable for use in the synthesis of ammonia, which comprises a vessel containing first and second catalyst beds through which a process stream of synthesis gas can pass radially in series, the beds being annular and arranged on a common annular axis; a heat exchanger positioned on the said axis in the centre of one of the catalyst beds; a first inlet for a first stream of synthesis gas; a second inlet for an exchange stream of synthesis gas and means whereby the exchange stream can pass to the heat exchanger; and means whereby the first stream and the exchange stream can be combined to form the process stream (which is cooled in the heat exchanger by the exchange stream).

2. Apparatus suitable for use in the synthesis of ammonia, which comprises a vessel containing first and second catalyst beds through which a process stream of synthesis gas can pass radially in series, the beds being annular and arranged on a common annular axis; a heat exchanger positioned on the said axis in the centre of one of the catalyst beds; a first inlet for a

first stream of synthesis gas; a second inlet for a shell stream of synthesis gas and means whereby the shell stream can pass inside the vessel and outside the catalyst beds; means whereby an exchange stream of synthesis gas can pass from a third inlet or from the shell stream to the heat exchanger; and means whereby the first stream, the exchange stream and, if separate from the exchange stream, the shell stream can be combined to form the process stream (which is cooled in the heat exchanger by the exchange stream).

3. Apparatus according to claim 2 in which there is a second heat exchanger, for indirect heat exchange between the process stream after its passage through the second catalyst bed and the shell stream.

4. Apparatus according to any preceding claim in which the axially positioned heat exchanger is positioned in the centre of the first catalyst bed through which the process stream passes.

5. Apparatus according to any preceding claim in which the streams which are combined to form the process stream are combined on the said annular axis.

6. Apparatus according to claim 1 substantially as described with reference to any of Figures 1 to 4 of the accompanying drawings.

7. Apparatus according to claim 1 substantially as herein described with reference to Figure 5 or Figure 6 of the accompanying drawings.

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FIG. 1

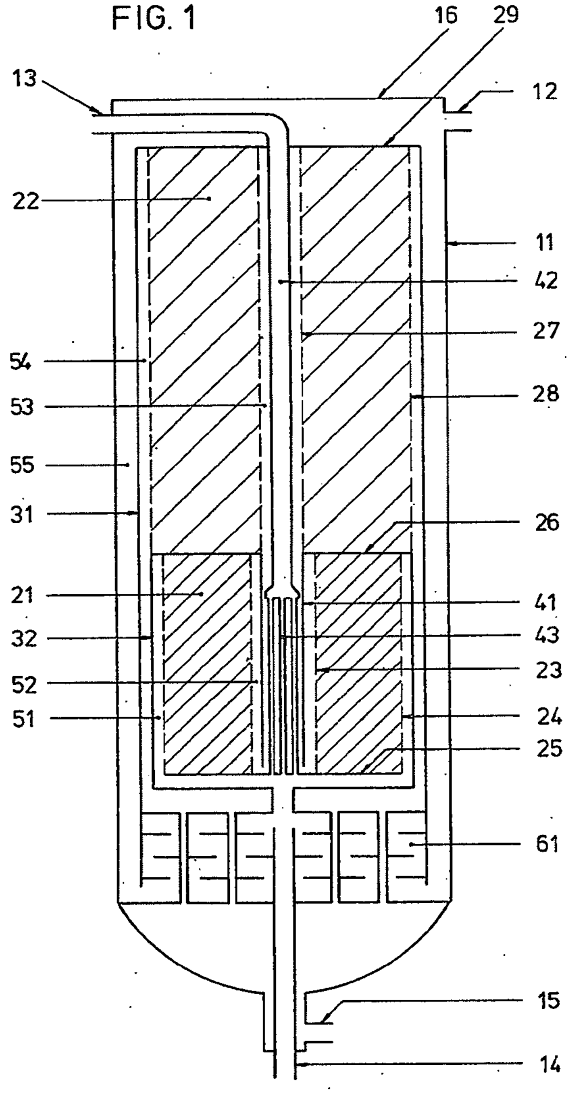
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FIG. 2

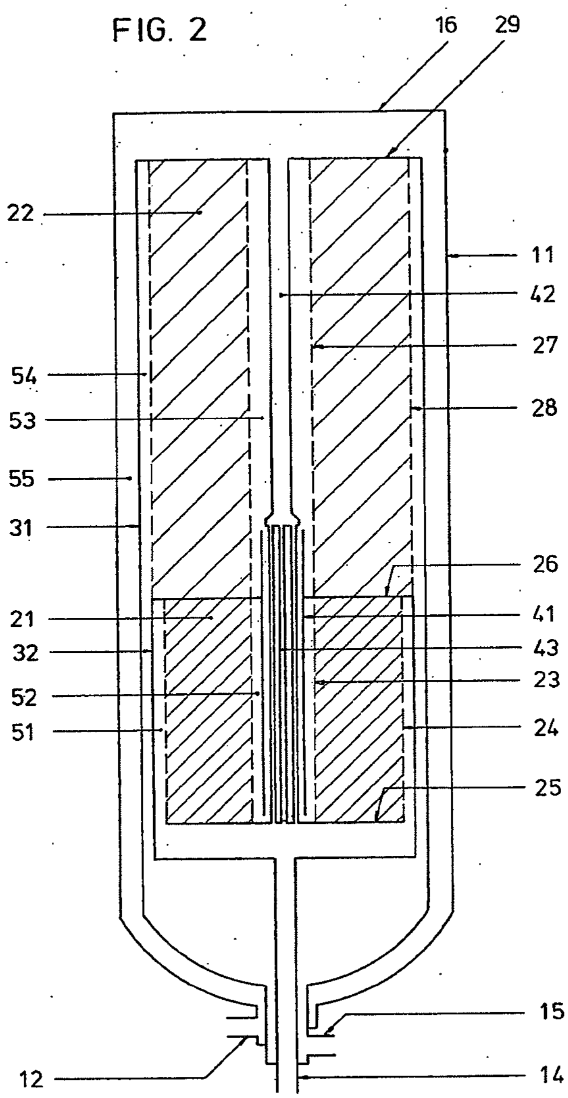


FIG. 3

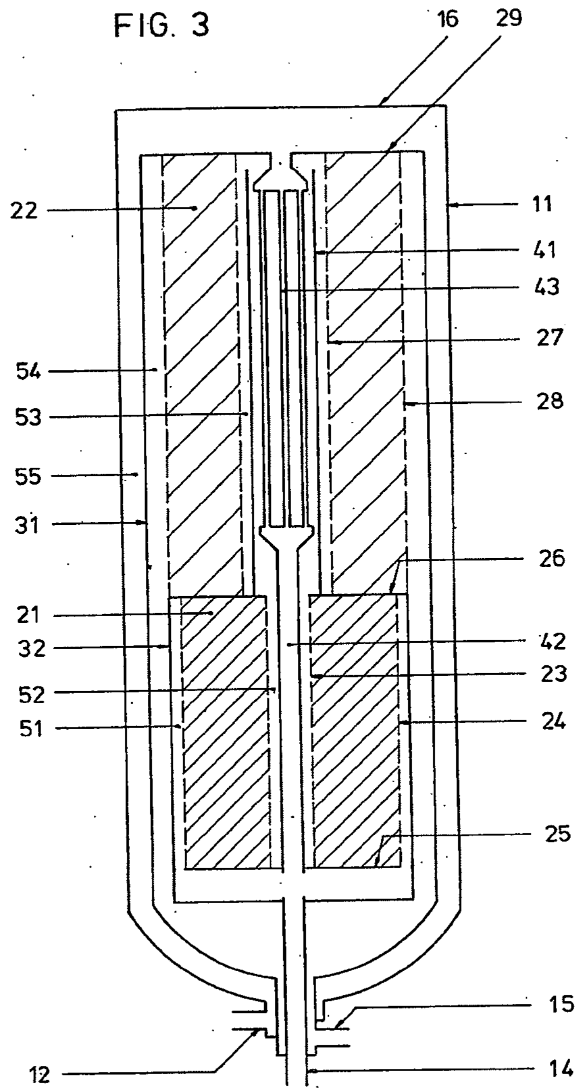
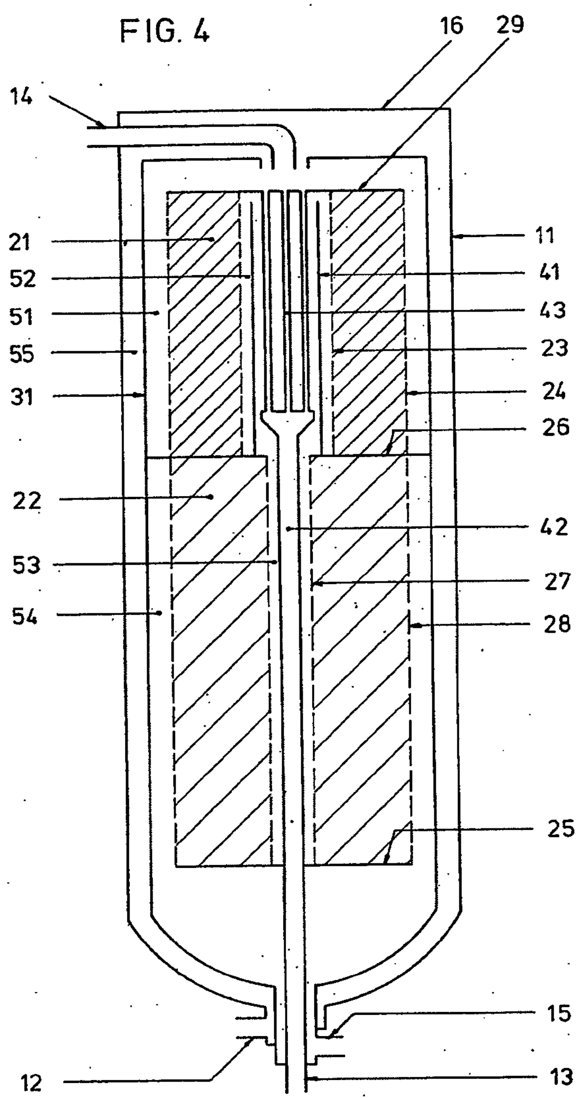


FIG. 4



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7 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 5

FIG. 5

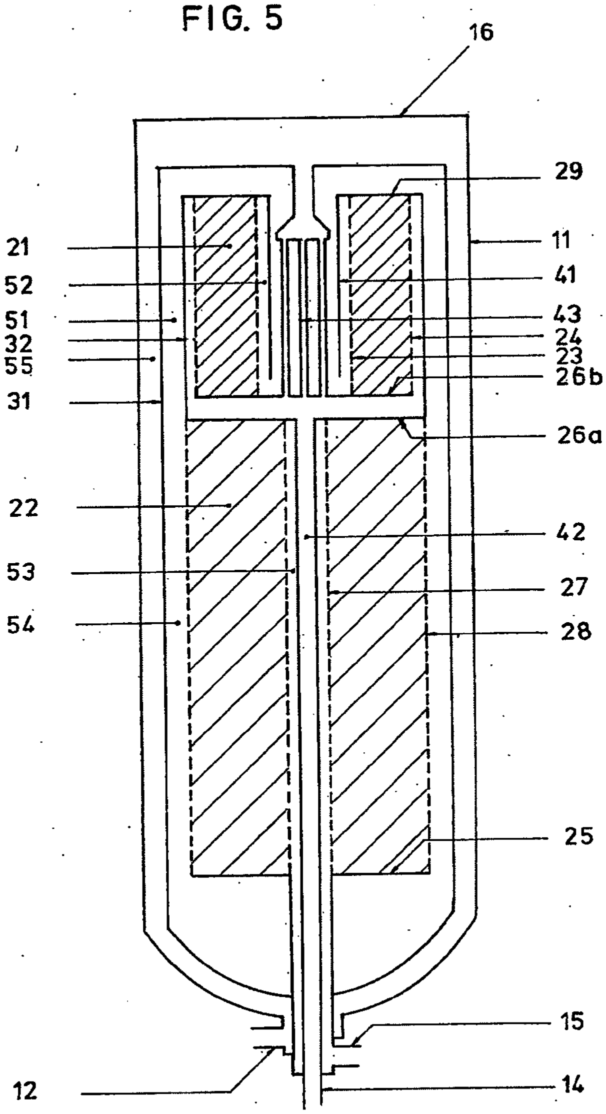

FIG. 6

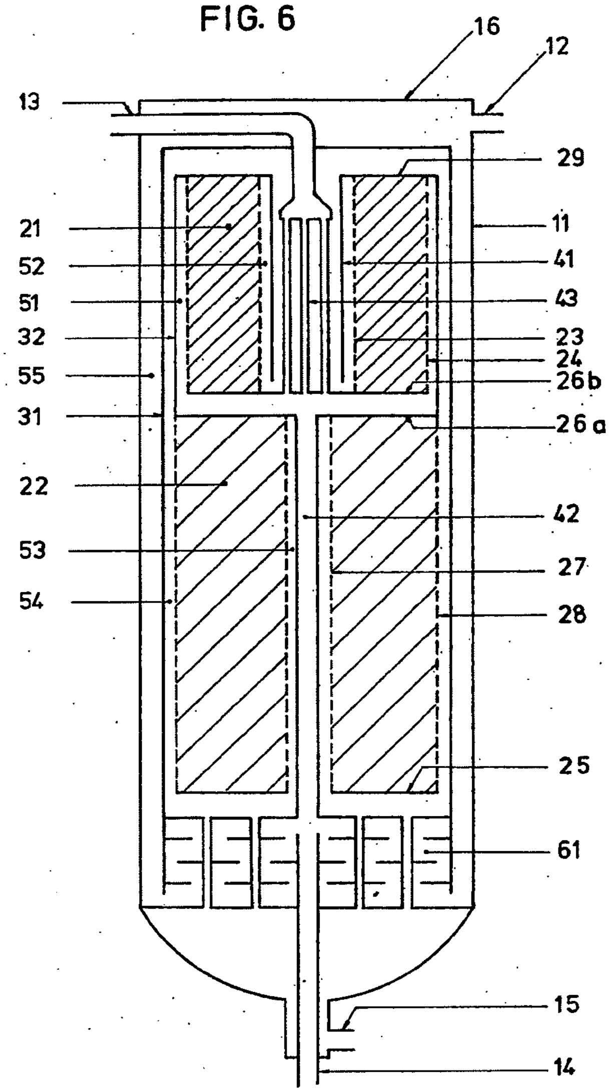
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FIG. 7